

# First-principles study of point defects at semicoherent interface

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Modeling semicoherent metal-metal interfaces has so far been performed using atomistic simulations based on semiempirical interatomic potentials. We demonstrate through more precise ab-initio calculations that key conclusions drawn from previous studies do not conform with the new results which show that single point defects do not delocalize near the interfacial plane, but remain compact. We give a simple qualitative explanation for the difference in predicted results that can be traced back to limited transferability of empirical potentials.

Nanostructured metallic multilayer composites (NMMC) are known to have superior mechanical properties compared to standard coarse grained metals [1] along with the ability to efficiently self-heal radiation damage [2, 3]. The latter is crucial for the material to inhibit creep and swelling in harsh environments. In order to utilize these materials in most effective manner, it is necessary to understand the underlying mechanisms leading to the aforesaid advantages. One route to accomplish that is via experiments where state of the art work has reached to a point where it is possible to engineer bulk nanostructured bi-metal multilayers while having control over structural features at atomic level which can considerably alter the mechanical properties and thermal stability of these materials [4].

Another way to gain insight into the way these materials behave during subjection to extreme mechanical or radiation environments is by theoretical means via computational methods. Since the time and length scales these processes cover are exceptionally widely spread, starting from attoseconds and picometers for electronic effects and going up to meters and years in continuum mechanics, there is no single equation or model that can currently cover all of this complexity. Therefore only a multi-scale modeling approach allows to eventually predict the properties and design optimal NMMCs for future industrial and energy technology applications.

This study concentrates on the atomic level part of the multi-scale method, where there has been considerable effort to model the structure and behavior of NMMCs in order to better understand the traits leading to the high tolerance to radiation damage. While the effects caused by irradiation are essentially macroscopic, they are still governed by changes in atomic level that can be traced back to single point defects. Therefore efforts have been directed to identifying possible lowest energy structures for the undamaged interfaces as well as describing the point defect properties such as configurations, formation

energies, migration barriers and mechanisms near the interfacial plane. Previous studies have shown that the interface does not support conventional point defects, that is vacancies and interstitial atoms, but instead pairs of extended jogs will form. Those delocalized defects have been shown to exhibit low formation energies and interaction through long-range forces [5]. This will also result in more complex migration pathways and recombination mechanisms than in bulk material [6–8].

The studies described above were performed using atomistic modeling based on classical molecular dynamics and empirical interatomic potentials which have a crucial role in determining the outcome of the simulations. Fitting empirical models to ab-initio or experimental data always presents the challenge of obtaining good transferability to the problem under study which often explores regions of phase space not used in the fitting process. For metallic systems the most widely utilized model is the embedded-atom method (EAM) developed by Daw and Baskes [9, 10]. Although there are alternatives, arguably having greater accuracy, it is still relevant because of its simplicity and computational scalability while providing relatively accurate description, especially for FCC metals.

There are two EAM potentials available for copper-niobium system which were fitted using two different methods. First by Demkowicz et al [11] (hereafter EAM1) uses modified Morse function for Cu-Nb interaction and has been fitted to dilute enthalpies of mixing and bulk modulus and lattice constant of hypothetical CuNb alloy in B2 structure. The second one by Zhang et al [12] (EAM2) uses more flexible polynomial-like function and is fitted to enthalpies of mixing of special quasirandom structures over the whole composition range with the aim of correctly reproducing experimental thermodynamics for the system.

In this work we show, that EAM1 and EAM2 give markedly different results for both the structure and en-

ergetics of point defects near the interface. Then we propose a solution to this discrepancy by relaxing the structures predicted by aforementioned two potentials using density-functional theory (DFT) calculations which essentially do not rely on empirical parameters thereby producing more accurate results. We then propose an explanation why some interatomic potentials might lead to erroneous characterization of the interface and how to possibly prevent this in future works.

All DFT calculations were done using plane-wave pseudopotential code Vienna Ab initio Simulation Package (VASP) [13–16] with supplied PAW pseudopotentials [17] and GGA-PBE approximation [18, 19]. For niobium the semi core  $p$  states were treated as valence. The cutoff energy for the plane waves was 273.214 eV. Single  $k$ -point ( $\Gamma$ -point) was used and smearing was handled by 1st order Methfessel-Paxton scheme [20] with width of  $\sigma = 0.01$  eV. Atomistic simulations were performed with classical molecular dynamics code LAMMPS [21].

The structure of the interface can be described by specifying the orientation of the surface normal to the interfacial plane and two parallel directions, one for each surface, that will be parallel when the interface is formed. It has been shown experimentally that copper-niobium interface forms predominantly in Kurdjumov-Sachs orientation [22]. In general calculating the energies of such structures using DFT is a complex task solely because of the number of atoms needed, and hence the required computational effort, to retain characteristic features and periodicities of the interface. The periodicity of the interface is defined by the locations of misfit dislocation intersections (MDIs), that is the areas where the atoms on each side of the interface overlap [23]. In case of copper and niobium in KS orientation the distances between the MDIs are relatively small enabling this specific interface to be modeled using a quasi-unit cell appropriately sized for DFT. This cell is an approximation and not a true unit cell for the larger system since albeit similar, the local environments around the MDIs are not equivalent. The setup is illustrated in Fig. 1.

In order to keep the calculations computationally feasible the number of atoms in the cell perpendicular to the interface must be limited. This results in two choices, either make the simulation box periodic or add vacuum in this direction. Former corresponds to having infinite number of thin alternating copper and niobium layers and latter to single interface and two free surfaces. We opted for having 1.65 nm layer of vacuum between the free surfaces. Unit cell vectors (in nm) for the resulting unit cell are  $a_x = (2.3, 0, 0)$ ,  $a_y = (0.75, 1.33, 0)$  and  $a_z = (0, 0, 3.0)$  and it consists of 216 Cu and 120 Nb atoms. We checked for possible errors by doubling the number of layers and calculating the structure, which did not change, and formation energy of vacancy, which reduced by 20 meV. While constructing a small unit cell using the method described above gives an appropriate rep-

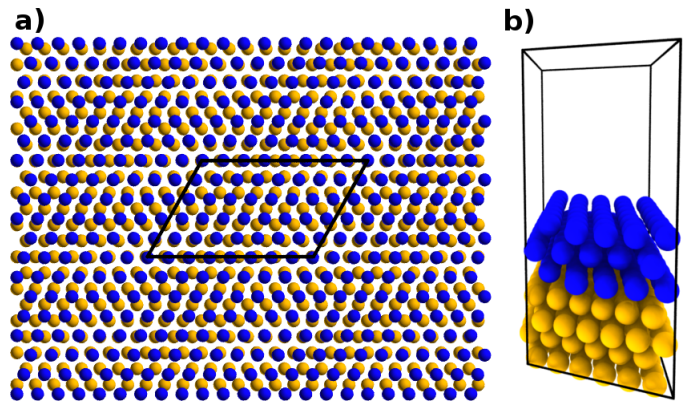


FIG. 1. Constructing small quasi-unit cell for Cu/Nb interface in Kurdjumov-Sachs orientation. Blue spheres represent niobium and yellow spheres copper atoms. (a) The unit cell is “cut out” from larger structure and has approximately same periodicity as the misfit dislocation intersections, that is the areas where copper and niobium atom positions coincide in  $x$ - and  $y$ -directions. (b) A 3D view of the simulation cell, where each layer consists of either 54 Cu or 40 Nb atoms. Total number of atoms is 336.

resentation of the undamaged interface, there is still the problem of finding ground state configurations of point defects. Therefore we calculated candidate structures using both EAM1 and EAM2 with molecular dynamics and then relaxed these using DFT. The ratio of lattice constants of Cu and Nb calculated using DFT and MD differ by less than 0.1% thereby making this method valid.

In order to a) check whether the vacuum layer or distortion of the true periodicity has any effect on the structure of the interface, b) to get input structures for DFT calculations and c) to assess whether relaxing the box has important effect on the outcome of the results, we first performed different molecular dynamics simulations with both EAM1 and EAM2. First the initial system was quenched from 600 K to 0 K followed by the energy minimization using conjugate gradient method. Next the copper atom with highest potential energy was removed and the process was repeated. A typical final structure as predicted by EAM1 is shown in Fig. 2a and has the same 4- and 5-atom rings as found in previous works while using EAM2 a compact single vacancy is formed. Relaxing the simulation box using EAM2 has minuscule effect on the formation energies while using EAM1 results in somewhat smaller energies. In either case the structural features are not affected.

Same process was carried out with single interstitial copper atom which was inserted into the interface after initial energy minimization next to the MDI. Again using EAM1 results in delocalization of the defect (on Fig. 3a) while EAM2 produces clear interstitial which resides between the copper and niobium layers.

Next all four structures were relaxed using DFT. The energy minimization was done using conjugate gradient

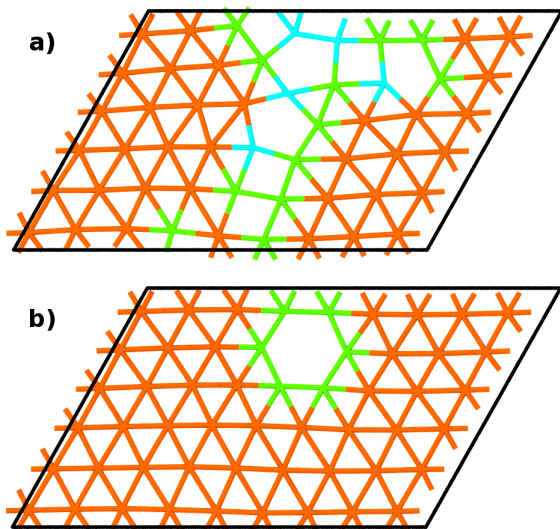


FIG. 2. Top view of interfacial copper layer with single vacancy at the interface before and after relaxing using DFT. (a) The structure was obtained by relaxing the interface with EAM1 which results in delocalization of the defect and formation of 4- and 5-atom rings. (b) Relaxing in DFT yields single compact vacancy. Lines and colors represent the in-plane bonds and coordination numbers respectively with orange being 6, green 5, cyan 4. The position of vacancy is at the MDI, but is shifted due to layers moving with respect to each other in simulation.

method until the maximum force on an atom was less than  $0.1 \text{ eV/\AA}$  while the energy difference between two sequential minimization steps was below  $0.1 \text{ meV}$ . The box size was kept constant for consistency and lower computational cost based on the fact that no change in structure and only negligible effect on formation energies was observed in constant pressure molecular dynamics runs using either EAM potential. Resulting structures are depicted on Fig. 2a and Fig. 3a for the vacancy and interstitial respectively. The final structures are very similar to the ones obtained with EAM2 potential, that is no delocalization happens and compact vacancy or interstitial is formed.

The formation energies for copper vacancies and interstitials at the interface calculated with the two potentials and DFT are listed in Table I. It must be noted though, that the values cannot be directly compared. The reason for that is the difference in defect energies of pure copper which will carry over to the formation energies of defects near the interface. Similarly, these values cannot be compared to the ones calculated using larger unit cell, firstly because of possible defect-defect interaction in neighboring cells due to periodicity and secondly due to the probable errors introduced by approximating the large cell using a smaller one. Moreover, while the defect delocalization predicted by EAM1 can result in diverse final structures with different energies as reported in Ref. [5], a single point defect has a well-defined formation en-

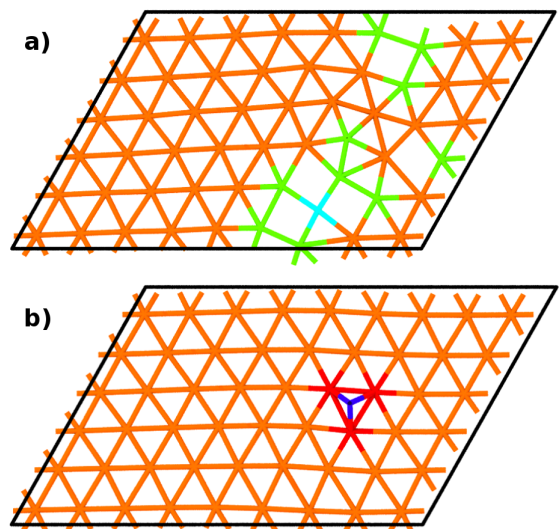


FIG. 3. Top view of interfacial copper layer with added interstitial atom before and after relaxing using DFT. (a) The structure was obtained by relaxing the interface with EAM1 potential which results in delocalization of the defect and formation of 4-atom rings. (b) After relaxing in DFT a single interstitial between the interfacial copper and niobium layers will emerge. Lines and colors represent in-plane bonds and coordination numbers respectively, with red being 7, orange 6, green 5 and cyan 4 and blue 3.

ergy.

Our results demonstrate that different empirical potentials can lead to contrasting results when the structures studied are substantially different from those used for the fitting procedure. The result of the fitting of alloy properties in case of EAM is a single function relating distance between two different species to the energy. Since the data used to fit EAM1 depends only on a small discrete set of distances, the energy function is also well defined only at these points. At the same time the energy of a semicoherent interface contains distances of nearly continuous spectrum which means that when using this method the energy of the interface and thus the formation energies of defects can take nearly arbitrary values limited only by the chosen functional form.

The same method of fitting as described above has been also used to “tune” the potentials to yield different enthalpies of mixing and to show how this would affect the behavior of vacancies and interstitials [24, 25]. While this method is a nice example of the ability of simulations to investigate scenarios which are impossible to achieve in experiments, having too small fitting database (too few distances in case of EAM) might again interfere with other physical quantities which can lead to incorrect conclusions.

A method has been proposed by Ercolessi and Adams in which instead of energies, forces are fitted to reproduce those obtained from first-principles calculations. This

TABLE I. Formation energies of copper vacancies and interstitials at the interface in eV. EAM1 tends to underestimate the formation energies while EAM2 overestimates these. Values in parentheses represent same energies in bulk copper. It must be noted, that a) since the energies are calculated using relatively small number of atoms, they do not truly represent formation energies in dilute limit and b) care must be taken comparing DFT and MD values since the energies in pure copper already differ.

Structure	EAM1 <sup>a</sup>	EAM2 <sup>b</sup>	DFT <sup>c</sup>
Vacancy	0.18 (1.26)	0.72 (1.27)	0.38 (1.17)
Interstitial	1.07 (3.27)	1.52 (3.09)	1.13 (3.86)

<sup>a</sup> Potential by Demkowicz et al [11]

<sup>b</sup> Potential by Zhang et al [12]

<sup>c</sup> This work

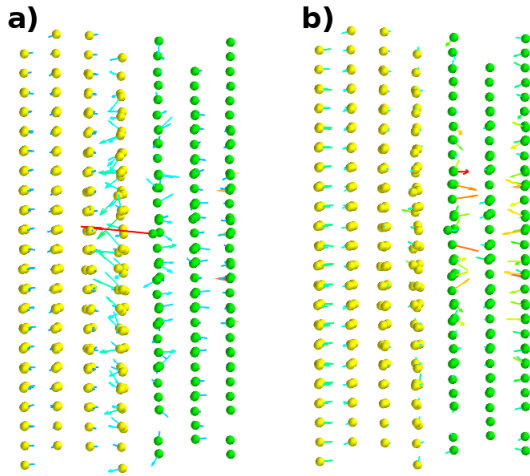


FIG. 4. Difference between DFT and MD forces (in arb. units) on atoms for DFT-relaxed interface structure with single copper vacancy. (a) and (b) show the forces obtained using EAM1 and EAM2 respectively. EAM1 produces significantly larger forces on copper atoms near the interfacial plane compared to those of DFT and EAM2. Copper atoms - yellow, niobium atoms - green.

has been shown to lead to greater accuracy and transferability of the potentials [26]. However, increasing the fitting database, as it is in the case of EAM2, can also result in significant improvement. Figure 4 shows the forces on atoms for the relaxed DFT structure with one vacancy calculated using both EAM1 and EAM2. The forces predicted by latter differ predominantly at free surfaces and for niobium atoms. It has been shown that it is quite hard or even impossible to accurately reproduce DFT forces for niobium using EAM [27] so this behavior is expected. With EAM1 the difference between DFT and MD forces for the first copper layer (where the vacancy is located) is much larger which leads to reconstruction of the layer and delocalization of the vacancy.

To summarize, we have shown that single compact point defects can exist at semicoherent metal-metal in-

terfaces without any delocalization contrary to results of previous studies. This could necessitate further investigation of defect migration, clustering and recombination. In addition, we have provided an explanation for the discrepancy between earlier atomistic studies and this work which can be attributed to different fitting strategies and intrinsic transferability limitations of empirical potentials.

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